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In re Japanese Application of

Yasuaki TSUCHIYA et al.

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for: "Chemical Mechanical Polishing Slurry"

VERIFICATION OF TRANSLATION

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Washington, D.C. 20231

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August 18, 2005

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[Title of the Invention] Chemical Mechanical Polishing Slurry

[Claims]

[Claim 1] A chemical mechanical polishing slurry comprising  
5 polishing grains, ammonium nitrate as an oxidizing agent, 1,2,4-triazole as a  
polishing promoter for a copper metal film and water in which pH is within a  
range of 3 to 4.

[Claim 2] The chemical mechanical polishing slurry as claimed  
in Claim 1 wherein a concentration of 1,2,4-triazole is within a range of 0.05  
10 to 5 wt%.

[Claim 3] The chemical mechanical polishing slurry as claimed  
in one of Claims 1 and 2 wherein a concentration of ammonium nitrate is  
within a range of 0.1 to 5 wt%.

[Claim 4] The chemical mechanical polishing slurry as claimed  
15 in one of Claims 1, 2 and 3 wherein a weight ratio of 1,2,4-triazole to  
ammonium nitrate (1,2,4-triazole concentration / ammonium nitrate  
concentration) is within a range of 0.01 to 5.

[Claim 5] The chemical mechanical polishing slurry as claimed  
in one of Claims 1 to 4 wherein the total of an ammonium nitrate and a  
20 1,2,4-triazole concentrations is 5 wt% or less.

[Claim 6] The chemical mechanical polishing slurry as claimed  
in one of Claims 1 to 5 comprising a silica as polishing grains wherein a  
content of the silica is within a range of 0.1 to 10 wt%.

[Claim 7] The chemical mechanical polishing slurry as claimed  
25 in one of Claims 1 to 6 wherein a polishing rate ratio of a copper film to a  
tantalum film (Cu polishing rate / Ta polishing rate) is 1/3 to 1/1.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Pertains]

This invention relates to a chemical mechanical polishing slurry  
5 for manufacturing a semiconductor device. In particular, it relates to a  
chemical mechanical polishing slurry suitable for forming a damascene  
copper-based metal interconnection comprising a tantalum-based metal as  
a barrier metal film material.

[0002]

10 [Prior Art]

With regard to forming a semiconductor integrated circuit such as  
ULSI which has been significantly refined and compacted, copper is a useful  
material for electric connection whereby a high-performance and highly  
reliable interconnection can be formed, because of its lower electrical  
15 resistance and good electromigration or stress-migration resistance.

[0003]

Since copper is less processable by dry etching, a copper  
interconnection has been formed by a so-called damascene process. For  
example, an electric connection such as an interconnection may be formed  
20 as described below.

[0004]

First, a concave such as a groove and a connection hole is  
formed on an insulating film formed on a silicon substrate. After forming a  
barrier metal film on the surface comprising the concave, a copper film is  
25 formed by plating such that the concave is buried. Then, the surface is  
polished to be flattened by chemical mechanical polishing (hereinafter,

referred to as "CMP") until the surface of the insulating film except the concave area is completely exposed. As a result, an electric connection such as a damascene interconnection, a via plug and a contact is formed, in which the concave is filled with copper via a barrier metal film.

5 [0005]

Generally, for forming a damascene type electric connection, a barrier metal film is formed as described above in order to prevent dispersion of a copper metal into an insulating film or improve adhesiveness of the copper metal to a substrate (insulating film). Examples of a suitable  
10 barrier metal film to a copper-based metal film include a tantalum-based metal such as Ta and TaN.

[0006]

Polishing such a copper-based metal film formed via a tantalum-based metal film, must be conducted, taking differences in  
15 polishing rates between the copper-based metal film and the tantalum metal and the insulating films into account.

[0007]

Since the concave in the insulating film must be buried, the copper-based metal film is formed as a thick film. A polishing slurry  
20 capable of polishing the copper-based metal film at a high speed is usually used for effectively polishing and removing the thick copper-based metal film. A polishing rate is, however, generally reduced when the polishing slurry is used for a tantalum-based metal film. As a result, when  
25 attempting to adequately polish and remove the tantalum-based metal film, the copper-based metal film in the concave is excessively removed, leading to dishing.

[0008]

Thus, for preventing such dishing, there has been proposed a two-step polishing process comprising a first polishing step for mainly polishing and removing the thick copper-based metal film for burying and a  
5 second polishing step for mainly polishing and removing the tantalum-based metal film.

[0009]

In the first polishing step, it is required to effectively polish and remove the thick burying copper-based metal film and to prevent dishing at  
10 the end of the first polishing step. In the second polishing step, it is required to effectively polishing not only a small amount of the residual burying copper-based metal film after the first polishing step but also the tantalum-based metal film and to flatten the polished surface using the insulating film as a stopper.

15 [0010]

In the second polishing step for mainly polishing and removing the tantalum-based metal film in such a two-step polishing process, a CMP slurry in which mechanical action contributes to polishing more than chemical action is generally used because the tantalum-based metal film is  
20 harder than the copper-based metal film. However, excessive mechanical polishing action for achieving an adequate polishing rate may cause excessive polishing of the insulating film and/or a rough polishing surface, so that a good electric connection cannot be formed. For preventing excessive polishing of the insulating film, it is effective to use a polishing  
25 slurry whose pH is adjusted to be acidic. However, it causes increase in chemical polishing action and thus increase in a polishing rate of the



burying copper-based metal film. As a result, it may increase a difference in a polishing rate between the copper and the tantalum-based metal films, leading to dishing and/or erosion.

[0011]

5 A commonly used CMP slurry comprises polishing grains, an oxidizing agent, a protective-film forming agent, an acid and water, and there have been various modifications for it in order to solve the above problems.

[0012]

10 Patent reference 1 (Japanese Laid-open Patent Publication No. 83780/1996) has described that ionization of copper by an oxidizing agent such as hydrogen peroxide and dishing in a CMP process may be prevented by using a polishing slurry containing benzotriazole or its derivative as a protective-film forming agent and forming a protective film on a copper film  
15 surface. Patent reference 2 (Japanese Laid-open Patent Publication No. 238709/1999) has also described that a triazole-based compound such as benzotriazole and 1,2,4-triazole is effective for preventing dishing. However, when using the conventional polishing slurry comprising the protective-film forming agent, there have been limitations to a covering  
20 amount of the copper film by the protective-film forming agent and to an inhibiting effect to polishing the copper film. Particularly, it has been difficult to inhibit polishing of the copper film in a strongly acidic range where copper tends to be oxidized.

[0013]

25 Patent reference 3 (Japanese Laid-open Patent Publication No. 85372/2001) has described a process wherein a polishing fluid comprising

an oxidizing agent, a protective-layer forming agent, an acid and water with a pH of 3 or lower may be used and a concentration of the oxidizing agent may be varied to adjust a polishing-rate ratio between a copper or copper-alloy film and a barrier metal film. Generally, a polishing rate for a copper-based metal film increases as a concentration of an oxidizing agent is increased, but a concentration of the oxidizing agent added must be carefully adjusted in an acidic range in which the copper metal film tends to be oxidized. That is, when a concentration level of the oxidizing agent in the polishing slurry is higher than a predetermined level even to minimal degree, the copper metal film is excessively polished. A desired polishing rate cannot be, therefore, achieved unless a concentration of the oxidizing agent is accurately adjusted. Hydrogen peroxide, a common oxidizing agent for a polishing slurry, tends to be deteriorated over time. Thus, it is added to and mixed with the polishing slurry by appropriate means such as a chemical blender immediately before use. However, it has been difficult to accurately and reproducibly adjust an oxidizing-agent concentration in such a process, particularly when a predetermined oxidizing-agent concentration is relatively lower.

[0014]

Patent reference 4 (Japanese Laid-open Patent Publication No. 89747/2001) has described a process wherein a polishing composition with a pH within a range of 3 to 6 and without an oxidizing agent may be used to reduce a polishing rate for a copper film. However, without an oxidizing agent at all, a polishing rate for a copper film is extremely low even in an acidic range in which copper tends to be oxidized, so that the copper film to be removed cannot be completely removed. The reference has also

described a method for controlling or regulate a polishing rate for a copper film by varying an amount of hydrogen peroxide added. However, as described above, it is difficult to adjust a polishing rate for a copper film to a desired rate by varying an amount of hydrogen peroxide added in a strongly  
5 acidic range in which copper tends to be oxidized.

[0015]

[Patent reference 1]

Japanese Laid-open Patent Publication No. 83780/1996

[Patent reference 2]

10 Japanese Laid-open Patent Publication No. 238709/1999

[Patent reference 3]

Japanese Laid-open Patent Publication No. 85372/2001

[Patent reference 4]

Japanese Laid-open Patent Publication No. 89747/2001

15 [0016]

[Problems to be solved by the Invention]

As described above, it has been difficult according to the prior art to adjust a polishing rate for a copper-based metal film within a desired range for preventing excessive polishing of the copper-based metal film in a  
20 strongly acidic range in which copper tends to be oxidized.

[0017]

An objective of this invention is to provide a chemical mechanical polishing slurry whereby a tantalum-based metal film for a barrier metal film can be polished and removed at an adequate rate, excessive polishing of a  
25 copper-based metal film for a damascene interconnection can be prevented and dishing can be minimized.

[0018]

[Means for solving the Problems]

This invention relates to a chemical mechanical polishing slurry comprising polishing grains, ammonium nitrate as an oxidizing agent, 1, 2, 5 4-triazole as a polishing promoter for a copper metal film and water and having a pH within a range of 3 to 4.

[0019]

[Modes for carrying out the Invention]

Hereinafter, preferred embodiments of the present invention will 10 be described.

[0020]

Examples of polishing grains which can be used in this invention include one or more selected from the group consisting of metal oxide polishing grains including aluminas such as  $\alpha$ -alumina,  $\theta$ -alumina,  $\gamma$  15 -alumina and fumed alumina; silicas such as fumed silica and colloidal silica; titania; zirconia; germania; and ceria. Among these, silica polishing materials such as colloidal silica and fumed silica are preferable in the light of prevention of excessive polishing in a copper-based metal film and/or scratches in a polished surface and stable dispersion in the slurry, and 20 particular preference is given to colloidal silica. An average particle size of a silica polishing material (an average particle size determined regarding a secondary particle as a single particle when secondary particles are contained) is preferably 10 nm or more, more preferably 20 nm or more while being preferably 100 nm or less, more preferably 80 nm or less, as 25 determined by light scattering diffraction method in the light of, for example, a polishing rate, dispersion stability and surface roughness of a polished

surface.

[0021]

A content of the polishing grain in a CMP slurry of this invention may be appropriately selected from the range of 0.1 to 10 wt%, based on  
5 the total amount of the CMP slurry, in the light of some factors such as polishing efficiency and polishing accuracy. Particularly, it is preferably 0.5 to 5 wt% in the light of a polishing rate, dispersion stability and a roughness in the polished surface.

[0022]

10 The CMP slurry of this invention comprises 1,2,4-triazole as a polishing promoter for a copper-based metal film. 1,2,4-Triazole may act as a complex forming agent and form a complex with copper ion within a pH range described below to promote ionization of copper. Furthermore, 1,2,4-triazole may be combined with ammonium nitrate described later to  
15 adjust a polishing rate of the copper-based metal film to a suitable level.

[0023]

A content of 1,2,4-triazole in this invention is preferably 0.05 wt% or more, more preferably 0.1 wt% or more to an overall CMP slurry while being preferably 5 wt% or less, more preferably 3 wt% or less. If a content  
20 of 1,2,4-triazole is too low, a polishing rate for a copper-based metal film is too low to adequately remove the copper-based metal film to be removed. Furthermore, if a content of 1,2,4-triazole is too high, dispersion stability is deteriorated.

[0024]

25 The CMP slurry of this invention comprises ammonium nitrate as an oxidizing agent. Ammonium nitrate properly oxidizes a copper-based

metal film within a pH range where copper tends to be oxidized, to ionize copper. Furthermore, 1,2,4-triazole described above may be combined to form a complex consisting of copper ion, nitrate ion and 1,2,4-triazole, resulting in promotion in copper ionization. Concentrations of ammonium  
5 nitrate and 1,2,4-triazole may be selected to adjust a polishing rate for a copper-based metal film within a suitable range.

[0025]

In the CMP slurry of this invention, a weight ratio of 1,2,4-triazole to ammonium nitrate (1,2,4-triazole concentration/ammonium nitrate  
10 concentration) is preferably 5 or less, more preferably 4 or less, further preferably 3 or less in the light of prevention of dishing and erosion due to excessive polishing of copper. The weight ratio is preferably 0.01 or more, more preferably 0.05 or more in the light of sufficient effects in combination of ammonium nitrate and 1,2,4-triazole.

15 [0026]

Using ammonium nitrate as an oxidizing agent provides the following advantages. When using an oxidizing agent such as hydrogen peroxide whose activity tends to be deteriorated over time, the oxidizing agent is generally added to and mixed with the CMP slurry by appropriate  
20 means such as a chemical blender immediately before use. In such a process, as a predetermined concentration of the oxidizing agent contained in the CMP slurry is lower, it becomes more difficult to reproducibly and accurately adjust an oxidizing agent concentration. In contrast, ammonium nitrate used in this invention is stable in the CMP slurry for a long period.  
25 Thus, it is not necessary to adding an oxidizing agent immediately before use. In other words, the agent can be contained in the slurry in advance

and a desired polishing rate for the copper-based metal film can be easily and reproducibly achieved.

[0027]

A content of ammonium nitrate in this invention is preferably 0.1  
5 wt% or more, more preferably 0.3 wt% or more while being preferably 5 wt%  
or less, more preferably 3 wt% or less. If a content of ammonium nitrate is  
too low, a polishing rate for a copper-based metal film is too low to  
adequately remove the copper-based metal film to be removed.  
Furthermore, if a content of ammonium nitrate is too high, dispersion  
10 stability is deteriorated.

[0028]

The total concentration of ammonium nitrate and 1,2,4-triazole in  
the CMP slurry of this invention is preferably 5 wt% or less, more preferably  
4 wt% or less, further preferably 3 wt% or less in the light of dispersion  
15 stability.

[0029]

The CMP slurry of this invention preferably has a pH within a  
range of 3 to 4. In a CMP slurry according to the prior art, 1,2,4-triazole is  
known to be a protective-film forming agent because it can be chemically  
20 adsorbed to an oxidized film formed in the surface of a copper-based metal  
film. However, within the pH range, 1,2,4-triazole can be combined with  
ammonium nitrate to promote ionization of copper and thus to promote  
polishing of the copper-based metal film. In a CMP using such a slurry, it  
is believed that ammonium nitrate properly ionizes the copper-based metal  
25 film while 1,2,4-triazole together with copper and nitrate ions forms a  
complex to promote ionization of copper.

[0030]

At a too high pH of the CMP slurry, a copper-based metal film tends to form an oxidized layer in its surface and 1,2,4-triazole forms a protective layer on the oxidized layer, to reduce a polishing rate for a copper-based metal film. On the other hand, at a too low pH of CMP slurry, an amount of an acid required for adjusting a pH is increased so that a concentration of the salt of 1,2,4-triazole with the acid used for adjusting a pH is increased. As a result, complex-forming ability of 1,2,4-triazole to copper is reduced, resulting in reduction in a polishing rate for the copper-based metal film. Furthermore, when using a silica polishing material as polishing grains, a pH substantially deviating from the range of 3 to 4 deteriorates dispersion stability in the silica polishing material.

[0031]

A pH of the CMP slurry can be adjusted using an acid or alkali according to a well-known method. Examples of an acid used in pH adjustment include inorganic acids such as nitric acid and sulfuric acid; organic acids such as formic acid and oxalic acid; and their salts. Examples of an alkali used in pH adjustment include alkali-metal hydroxides such as sodium hydroxide and potassium hydroxide; alkali-metal carbonates such as sodium carbonate and potassium carbonate; ammonia; and amines.

[0032]

The CMP slurry of this invention may comprise a variety of additives such as dispersants, buffers and viscosity modifiers commonly used in a polishing slurry as long as they do not deteriorate the properties of the slurry.

[0033]



A polishing slurry of this invention may be prepared by a common process for preparing a free-grain aqueous polishing slurry. For example, to an aqueous solvent are added a proper amount of the polishing material and, if necessary, a proper amount of a dispersing agent for dispersion. In  
5 such a dispersion process, an appropriate apparatus may be, if necessary, used, including an ultrasonic disperser and a bead mill. The other components may be added and mixed before or after dispersion.

[0034]

CMP using a polishing slurry of this invention may be conducted,  
10 using, for example a procedure described below. First, a substrate is prepared, on which an insulating film is formed, a concave with a given pattern is formed on the insulating film and a tantalum-metal and a copper-metal films are deposited on the concave. The substrate is placed on a wafer carrier such as a spindle. The metal film surface to be polished  
15 in the substrate is contacted with a polishing pad attached on a surface plate such as a rotary plate under predetermined pressure. While supplying a polishing slurry between the substrate and the polishing pad, polishing is initiated by relatively moving the wafer and the polishing pad (e.g., rotating both). The polishing slurry may be supplied on the polishing  
20 pad from a separate supply pipe or from the surface plate side. If necessary, a pad conditioner is contacted with the surface of the polishing pad to condition the surface of the polishing pad.

[0035]

A polishing slurry of this invention described above may be  
25 effectively used when polishing by CMP is conducted to a copper-based metal film on a substrate comprising an insulating film having concaves

such as grooves and connection holes in which the copper metal film is formed over the whole surface of the barrier metal film such the concaves are buried, to form an electric connection such as a damascene interconnect, a via plug and a contact. Examples of an insulating film  
5 include a silicon oxide film, a BPSG film, an SOG film, an SiOF film, an HSQ film, an SiOC film, an MSQ film, a polyimide film, a parilen film, a Teflon film and an amorphous carbon film. Examples of a barrier metal film suitable for a copper-based metal film, i. e., a copper film or a copper-alloy film mainly comprising copper include those made of a tantalum-based metal  
10 such as tantalum, tantalum nitride and tantalum nitride silicon.

[0036]

The CMP slurry of this invention can be effectively used in a step from initiation of polishing of the tantalum-based metal film to final polishing and removing the tantalum-based metal film except the concaves to form an  
15 electric connection. It can be suitably used in the second polishing in the above two-step polishing process.

[0037]

A composition ratio of the CMP slurry of this invention may be preferably adjusted such that a polishing rate for the copper-based metal  
20 film is preferably 20 nm/min or more, more preferably 30 nm/min or more while being preferably 100 nm/min or less, more preferably 90 nm/min or less, particularly preferably 80 nm/min or less. If a polishing rate for the copper-based metal film is too low, a copper-based metal film to be removed tends to remain and a throughput may be reduced. On the  
25 contrary, if a polishing rate for the copper metal film is too high, dishing or erosion tends to occur due to excessive polishing. A composition ratio of

the CMP slurry of this invention may be desirably adjusted such that a polishing rate for the tantalum-based metal film is preferably 40 nm/min or more, more preferably 60 nm/min or more while being preferably 200 nm/min or less, more preferably 150 nm/min or less. If a polishing rate for the tantalum-based metal film is too low, a tantalum-based metal film to be removed tends to remain and a throughput may be reduced. On the contrary, if a polishing rate for the tantalum-based metal film is too high, an insulating film may be excessively polished or a polished surface may be coarse.

10 [0038]

A ratio of a polishing rate for the copper-based metal film to that for the tantalum metal film (Cu/Ta polishing rate ratio) is preferably 1/3 to 1/1 in the light of preventing excessive polishing of the copper-based metal film and minimizing dishing and erosion while adequately polishing and removing the film. For example, CMP may be conducted using a slurry which has been prepared such that a polishing rate for the copper film is 20 to 100 nm/min and a ratio of the polishing rate for the copper film to that for the tantalum film (Cu polishing rate / Ta polishing rate) is 1/3 to 1/1, to form an excellent damascene copper interconnection.

20 [0039]

[Examples]

Hereinafter, this invention will be further specifically described with reference to Examples.

[0040]

25 (CMP conditions)

CMP was conducted using a polisher (Speedfam Co. Ltd., SH-24).

The polisher comprised a surface plate on which a polishing pad with a diameter of 61 cm (Rodel-Nitta Company, IC 1400) was attached.

Polishing conditions were as follows: a polishing-pad contact pressure: 27.6 kPa; a polishing-pad polishing area: 1820 cm<sup>2</sup>, a rotating speed of the surface plate: 80 rpm; a carrier rotating speed: 80 rpm; and a polishing slurry feeding rate: 100 mL/min.

[0041]

The substrate to be polished was an Si substrate on which a copper or a tantalum films had been deposited by sputtering.

10 [0042]

(Determination of a polishing rate)

A polishing rate was estimated from surface resistivity values before and after polishing. Four needle electrodes were aligned on a wafer with a given interval. A given current was applied between the outer two probes to detect a potential difference between two inner probes for determining a resistance (R') and further the value is multiplied by a correction factor RCF (Resistivity Correction Factor) to obtain a surface resistivity ( $\rho_s'$ ). A surface resistivity ( $\rho_s$ ) is determined for a wafer film whose thickness (T) (nm) is known. The surface resistivity is inversely proportional to the thickness. Thus, when a thickness for a surface resistivity of  $\rho_s'$  is d, an equation:

$$d(\text{nm}) = (\rho_s \times T) / \rho_s'$$

holds true. Using the equation, the thickness d can be determined.

Furthermore, a variation of thickness between before and after polishing was divided by a polishing time to estimate a polishing rate. A surface resistivity was determined using a surface resistance detector (Mitsubishi

Chemical Corporation, Four Probe Resistance Detector, Loresta-GP).

[0043]

(Preparation of a CMP slurry)

As shown in Tables 1 to 4, slurries comprising 3 wt% of a colloidal  
5 silica (Tama Chemical Co.Ltd., TOSL series, a primary particle size: about  
70 nm) , 1,2,4-triazole (available from ACROS), ammonium nitrate  
(available from KANTO KAGAKU) was prepared as Examples and  
Comparative Examples. Furthermore, CMP slurries of comparative  
examples were prepared, which comprised benzotriazole (KANTO  
10 KAGAKU) or glycine (KANTO KAGAKU) instead of 1,2,4-triazole and  
hydrogen peroxide instead of ammonium nitrate, respectively. Hydrogen  
peroxide was introduced into the slurries by adding and mixing 30 wt%  
aqueous hydrogen peroxide (KANTO KAGAKU) to the slurries. The CMP  
slurries thus prepared were used for CMP under the above conditions.

15 [0044]

(Examples 1 to 3 and Comparative Examples 1 to 8)

As is obvious from the results in Examples 1 to 3 and  
Comparative Examples 1 and 2 shown in Table 1, the CMP slurries  
comprising 1,2,4-triazole and ammonium nitrate provided an increased  
20 copper polishing rate at a pH within a range of 3 to 4 while a practical  
polishing rate for copper was not obtained a pH deviating the range of 3 to  
4.

[0045]

As is obvious from Comparative Examples 3 to 8 shown in Table  
25 1, the slurries comprising benzotriazole or glycine instead of 1,2,4-triazole  
provided a substantially constant polishing rate for copper at a pH of 2.5 to

5, which was not practically useful.

[0046]

These results indicate that a suitable polishing rate for a copper film can be obtained using the CMP slurries in Examples 1 to 3 comprising 1,2,4-triazole and having a pH within a range of 3 to 4.

[0047]

(Examples 1, 4 to 6 and Comparative Example 9)

As is obvious from the results in Examples 1, 4 to 6 shown in Table 2, the higher a concentration of 1,2,4-triazole was, the higher a polishing rate for copper was. In contrast, when using the CMP slurry without 1,2,4-triazole in Comparative Example 9, a suitable polishing rate for a copper film could not be obtained.

[0048]

These results indicate that without 1,2,4-triazole, a suitable polishing rate for copper cannot be obtained in the presence of ammonium nitrate and that a polishing rate for copper can be adjusted by varying a 1,2,4-triazole concentration.

[0049]

(Examples 1, 7 to 9 and Comparative Example 10)

As is obvious from the results in Examples 1, 7 to 9 shown in Table 3, the higher a concentration of ammonium nitrate was, the higher a polishing rate for copper was. In contrast, when using the CMP slurry without ammonium nitrate in Comparative Example 10, a suitable polishing rate for a copper film could not be obtained.

[0050]

These results indicate that without ammonium nitrate, a suitable

polishing rate for copper cannot be obtained in the presence of 1,2,4-triazole and that a polishing rate for copper can be adjusted by varying an ammonium nitrate concentration.

[0051]

5 (Example 10 and Comparative Examples 11 and 12)

As is obvious from the results of Example 10 shown in Table 4, a suitable polishing rate ratio was obtained at an oxidizing agent (ammonium nitrate) concentration of 1 wt%. In contrast, using hydrogen peroxide as an oxidizing agent (Comparative Examples 11 and 12), a suitable polishing rate ratio was not obtained even when reducing an oxidizing agent concentration to 0.05 wt%. These results indicate that this invention can provide a desired polishing rate ratio and a CMP slurry in which an oxidizing agent concentration can be easily adjusted to a desired level.

[0052]

15

[Table 1]

	Polishing material (wt%)	Oxidizing agent (wt%)	Complex forming agent (wt%)	pH	Cu polishing rate (nm/min)
Example 1	Colloidal silica (3)	Ammonium nitrate (1.0)	1,2,4-Triazole (0.5)	3.5	48
Example 2	Colloidal silica (3)	Ammonium nitrate (1.0)	1,2,4-Triazole (0.5)	3	42
Example 3	Colloidal silica (3)	Ammonium nitrate (1.0)	1,2,4-Triazole (0.5)	4	35
Comp. Exam. 1	Colloidal silica (3)	Ammonium nitrate (1.0)	1,2,4-Triazole (0.5)	2.5	10
Comp. Exam. 2	Colloidal silica (3)	Ammonium nitrate (1.0)	1,2,4-Triazole (0.5)	5	14
Comp. Exam. 3	Colloidal silica (3)	Ammonium nitrate (1.0)	Benzotriazole (0.5)	3.5	9
Comp. Exam. 4	Colloidal silica (3)	Ammonium nitrate (1.0)	Benzotriazole (0.5)	2.5	10
Comp. Exam. 5	Colloidal silica (3)	Ammonium nitrate (1.0)	Benzotriazole (0.5)	5	5
Comp. Exam. 6	Colloidal silica (3)	Ammonium nitrate (1.0)	Glycine (0.5)	3.5	14
Comp. Exam. 7	Colloidal silica (3)	Ammonium nitrate (1.0)	Glycine (0.5)	2.5	11
Comp. Exam. 8	Colloidal silica (3)	Ammonium nitrate (1.0)	Glycine (0.5)	5	9

[0053]

[Table 2]

	Colloidal silica (wt%)	Ammonium nitrate (wt%)	1,2,4-Triazole (wt%)	pH	Cu polishing rate (nm/min)
Example 4	3	1.0	0.1	3.5	24
Example 1	3	1.0	0.5	3.5	48
Example 5	3	1.0	1.0	3.5	59
Example 6	3	1.0	2.0	3.5	89
Comp. Exam. 9	3	1.0	None	3.5	14



[0054]

[Table 3]

	Colloidal silica (wt%)	Ammonium nitrate (wt%)	1,2,4-Triazole (wt%)	pH	Cu polishing rate (nm/min)
Example 7	3	0.1	0.5	3.5	21
Example 8	3	0.5	0.5	3.5	45
Example 1	3	1.0	0.5	3.5	48
Example 9	3	2.0	0.5	3.5	57
Comp. Exam. 10	3	None	0.5	3.5	9

[0055]

[Table 4]

	Polishing material (wt%)	Oxidizing agent (wt%)	Complex forming agent (wt%)	pH	Cu polishing rate (nm/min)	Ta polishing rate (nm/min)	Cu/Ta polishing rate ratio
Exam. 10	Colloidal silica (3)	Ammonium nitrate (1.0)	1,2,4-Triazole (0.5)	3.5	48	84	0.57
Comp. Exam. 11	Colloidal silica (3)	Hydrogen peroxide (0.2)	1,2,4-Triazole (0.5)	3.5	241	79	3.07
Comp. Exam. 12	Colloidal silica (3)	Hydrogen peroxide (0.05)	1,2,4-Triazole (0.5)	3.5	99	83	1.19

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[0056]

#### [Effect of the Invention]

As is obvious from the above, a CMP slurry of this invention can be used to easily adjust a polishing rate for a copper-based metal film even in a strongly acidic range where the copper-based metal film tends to be oxidized. Therefore, in a process where a copper-based metal film and a tantalum-based metal film are simultaneously polished to form a damascene interconnection of the copper-based metal film, a suitable polishing rate ratio of the copper-based metal film to the tantalum-based metal film can be obtained and thus dishing or erosion can be minimized.

[Document Name] Abstract

[Abstract]

[Problems] An objective of this invention is to provide a chemical mechanical polishing slurry whereby a tantalum-based metal film for a barrier metal film can be polished and removed at an adequate rate, excessive polishing of a copper-based metal film for a damascene interconnection can be prevented and dishing can be minimized.

[Means for Solving the Problems] This invention relates to a chemical mechanical polishing slurry comprising polishing grains, ammonium nitrate as an oxidizing agent, 1,2,4-triazole as a polishing promoter for a copper metal film and water and having a pH within a range of 3 to 4.

[Chosen Drawing] none